ELSEVIER

Journal of Photochemistry and Photobiology A: Chemistry 117 (1998) 149–152

Journal of Photochemistry and Photobiology A:Chemistry

Preparation and photoconductivity study of TiOPc nanometer particles

H.Z. Chen*, K.J. Jiang, M. Wang, S.L. Yang

Institute of Polymer Science and Materials, State Key Lab of Silicon Materials, Zhejiang University, Hangzhou 310027, China

Received 5 January 1998; received in revised form 15 May 1998; accepted 16 June 1998

Abstract

Oxotitanium phthalocyanine (TiOPc) nanometer particles dispersed in polycarbonate (PC) resin are obtained successfully by the method of mechanical sand grinder. The mean grain sizes of TiOPc particles and the particle morphology are measured by particle size analyzer and TEM. The xerographic properties of TiOPc nanometer particles are investigated in function-separated single-layer photoreceptors that consist of TiOPc nanometer particles as the charge-generation material (CGM) and α-naphthalic hydrazone (α-NH) as the charge-transportation material (CTM). It is found that the photosensitivity of the function-separated single-layer photoreceptor is higher than that of the double layer device (same CGM and CTM). The photoconductivity–particle size relationship study shows that the smaller the particle size of TiOPc, the better the photoconductivity, which may result from the large specific surface area of the TiOPc nanometer particles.

Keywords: Photoconductivity; Oxotitanium phthalocyanine; Nanometer particle; Single-layer photoreceptor

1. Introduction

Photoconductive material is a new type of high technology information material which can generate e–h pairs upon illumination. It has been extensively used in copier application, laser printer, and digital xerography [1]. Organic photoconductive materials have shown their special position because of their non-toxicity, low cost, magnitude and variability of development, panchromaticity, mechanical and architectural flexibility [2]. Oxotitanium phthalocyanine (TiOPc), as an organic molecular crystal, has been developed as a charge generation material (CGM) of photoreceptor with a high near-IR sensitivity [3]. The relation between the grain size of TiOPc and photoconductivity, however, has not been studied.

Recently, the literature has reported on nanometer materials because of their unique characteristics. Most of the materials studied are inorganic materials, such as metals, oxides and non-metals, which are formed by metal bond or covalent bond. Very few reports are about the preparations of nanometer particles in organic molecular crystals. Wang and Herron think that weak intermolecular interactions in the organic molecular crystals rarely extend beyond the nearest neighbours and the electronic properties of molecular crystals are usually independent on the size of the crystal [4]. However, Koyman et al. and Law et al. found that the photoconductivity of the organic azo pigment depended on the size of the crystal [5,6]. Nanoscaled size effects on photoconductivity of conjugated polymers are also observed by Zhang et al. [7].

So far, three kinds of methods have been developed to prepare nanometer particles: vapour phase, liquid phase, and solid phase. Mechanical sand grinder is one of the solid phase methods, but particles prepared by this method are especially easy to coagulate. In this paper, we use polymer resin, in which the nanometer particles are embedded during grinding, to avoid particle aggregation.

The most current commercial photoreceptors (P/Rs) are made in function-separated double-layer structure (see Fig. 1(a)). Here a function-separated single-layer photoreceptor (Fig. 1(b)) is put forward. The function-separated single-layer P/R owns the advantages of lower cost, simplified equipment and fabrication technology, and may be a promising approach. In this paper, the single-layer P/R is made from the dispersion system of TiOPc nanometer particles, which are used as the CGM, and hydrazone, which is used as the CTM. The photoconductivity study shows that photosensitivity depends on the size of TiOPc nanometer particles.

---

*Corresponding author. Fax: +86-571-5100141

1010-6030/98/$ – see front matter
PII: S1010-6030(98)00325-6

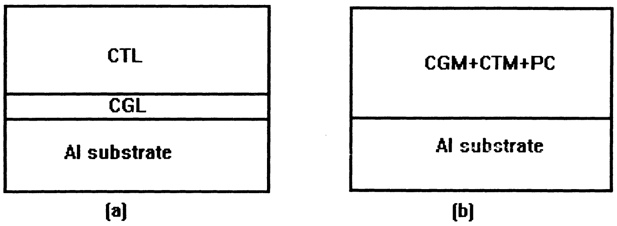


Fig. 1. Structures of (a) function-separated double-layer photoreceptor (b) function-separated single-layer photoreceptor.

2. Experimental

2.1. Materials

TiOPc was synthesized and purified in our lab according to the literature [8]. Polycarbonate (PC) was obtained from the Chemical Engineering Factory of Shanghai (China) and purified by precipitation by adding absolute alcohol into its chloroform solution. α-NH from the Tianjin Institute of Reprographic Technology (China) was purified by recrystallizing twice from absolute alcohol. Tetrahydrofuran (THF) and the other reagents were commercially available and of analytical grade.

2.2. Preparation of TiOPc nanometer particles

Quantitative TiOPc, polycarbonate (PC), glass balls (Φ1 mm + Φ2 mm 1:1 by wt.), and THF were added into a 100 ml flask. The suspension was stirred at 25°C for 2 h, then filtrated to remove the glass balls, and the dispersion system containing TiOPc nanometer particles embedded in PC resin was obtained.

2.3. Particle size analysis

The dispersion system prepared above was used directly to detect the particle size of TiOPc on LS230 Laser Particle Size Analyzer (Coulter, USA).

2.4. Transmission Electron Microscopy

A piece of copper net was dipped into the dispersion made in 2.2, dried in air, and then used to record the image of TiOPc nanometer particles on a Hitachi 600-4 Transmission Electron Microscopy (TEM).

2.5. Fabrication of function-separated single-layer photoreceptor

The dispersion solution containing TiOPc nanometer particles embedded in PC resin was added to the THF solution dissolving α-NH and PC. The mixed suspension was coated onto an aluminium plate with a thickness of about 30 μm, and a function-separated single-layer photoreceptor (P/R) was fabricated which consisted of TiOPc nanometer particles as CGM and α-NH as CTM (Fig. 1(b)). The ratio of TiOPc, α-NH and PC is 1:14:10 by weight.

2.6. Photoconductivity measurement [9,10]

The xerographic properties of TiOPc nanometer particles were measured on a GDT-II model photoconductivity measuring device by the xerographic photodischarge method. Near infrared light of 700–850 nm was applied as a light source. In the measurement, the surface of the P/R was negatively charged in the dark by corona charging at first, then the surface charges were cancelled out by charge carriers generated in CGM when the P/R was exposed to light. From this procedure, we could obtain ΔV_1, which was a percentage of the potential discharge after 1 s of exposure, $t_{1/2}$, which was the half-discharge time, and $E_{1/2}$, which was the half-discharge exposure energy and equaled the product of exposure intensity I and $t_{1/2}$. These three parameters can indicate the photosensitivity of the P/R. The lower the $t_{1/2}$ and $E_{1/2}$ values, and the bigger the ΔV_1 value, the higher the photosensitivity.

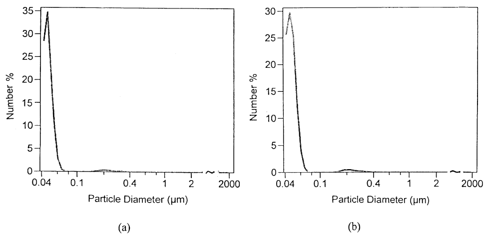
3. Results and discussion

3.1. Characterization of TiOPc nanometer particles

TiOPc particle size analyses may be seen from Fig. 2. Both curve *a* and *b* show a strong peak at about 50 nm, a very weak peak at about 200 nm. From the number statistics, the particle size mean value of TiOPc particles is 51.7 and 52.6 nm, respectively, and the particle diameter of more than 90% TiOPc particles is smaller than 55.6 nm (curve a) or 56.9 nm (curve b). These values indicate that nanometer-sized TiOPc is, indeed, obtained and the method of mechanical sand grinder by embedding TiOPc particles in PC resin is available to prepare nanometer sized TiOPc particles.

Fig. 3 shows the TEM micrograph from the TiOPc nanometer particle sample. The image reveals the ball-shaped microcrystals with a size of 20–60 nm. It is the embedding effect of PC resin that prevents the TiOPc microcrystals from aggregating into a large size.

Stability of the nanometer-sized TiOPc particles embedded in PC resin is investigated (see Table 1). As shown in Table 1, after 42 days, the mean values of the



(a) (b)

Fig. 2. Particle size distribution of nanoscaled TiOPc.

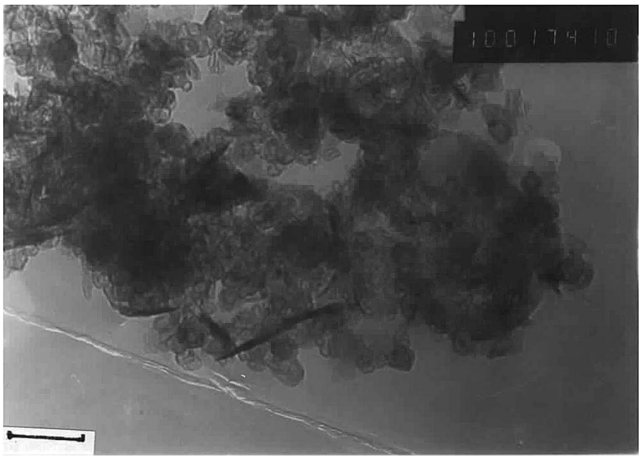


Fig. 3. TEM micrography from TiOPc nanometer particles. Scale bar: 100 nm.

Table 1
Stability of nanometer-sized TiOPc particles

Sample	Average particle size (nm) immediately after dispersion	Average particle size (nm) after preservation for 42 days
1	52	55
2	54	57

TiOPc particles become to 55.1 and 57.6 nm from 51.7 and 54.3 nm, respectively, proving good stability of TiOPc nanometer particles.

3.2. Photoconductivity

Table 2 lists the photoconductivities of single-layer P/Rs for various TiOPc nanometer particles. To TiOPc with average particle size of 52 nm, the surface-charged potential (V_o) reaches 789 V under the exposure of 20 lux light intensity, the residual potential (V_r) is zero, the percentage of potential discharge after 1 s of exposure is as high as 100%, the half-discharge time ($t_{1/2}$) is only 0.125 s, and the half-discharge energy ($E_{1/2}$) is as small as 2.5 lux. s, indicating high photosensitivity. Other nanometer-sized TiOPc samples (53–89 nm) also exhibit good charge acceptance (V_o=789–820 V), low residual potential (V_r=7–39 V) and dark discharge rate (Rd=26–31V/s), as well as high ΔV_1 values (97–100%) and low $t_{1/2}$ (0.125–0.250 s) and $E_{1/2}$ (2.5–5.0 lux. s) values. All these observations suggest that nanometer-sized TiOPc owns excellent photoconductivity.

By comparison, the single-layer P/Rs were made from TiOPc with average particle size of 251 and 281 nm. As shown in Table 2, they have bigger ΔV_r, lower ΔV_1, longer $t_{1/2}$, and higher $E_{1/2}$, when compared to those of nanosized TiOPc, indicating worse photoconductivity. A three-fold increase in photosensitivity (from 7.5 to 2.5 lux. s) is observed when the average particle size of TiOPc is reduced from 281 nm to 52 nm. That is to say, photoconductivity increases with decreasing particle size of TiOPc. The smaller the particle size of TiOPc, the better the photoconductivity.

Photogeneration mechanism study of azo pigments in function-separated double-layer P/Rs shows that the photocarriers are generated at the CGM/CTM interface resulted from the CTM penetration into the CGL [11,12]. Following this argument, it may be suggested that the larger the surface area of the CGM/CTM interface, the more the photocarrier's generation sites, and consequently the higher the photosensitivity. For our particular single-layer P/Rs consisting of TiOPc fine particles (CGM) embedded in α-NH (CTM), there is no doubt that the surface area of the CGM/CTM interface increases by decreasing the size of TiOPc particles. So it is easy to understand that photosensitivity is enhanced with the decreasing size of TiOPc particles in the single-layer P/R. This observation agrees well with the result of Law's studies on azo pigments in the double-layer devices [6].

Table 2
Relationship between particle size and photoconductivity of P/Rs from TiOPc

Sample	Average particle size (nm)	P/R	V_o (V)	V_r (V)	Rd (V/s)	ΔV_1 (%)	$t_{1/2}$ (s)	I (lux)	$E_{1/2}$ (lux. s)
1	52		−789	0	26	100	0.125	20	2.5
2	53		−820	−7	28	100	0.125	20	2.5
3	68		−796	−23	31	100	0.188	20	3.8
4	74	S-L	−789	−39	28	97	0.250	20	5.0
5	89		−789	−31	28	97	0.250	20	5.0
6	251		−890	−85	31	92	0.312	20	6.2
7	281	S-L	−707	−35	29	88	0.250	30	7.5
8	281	D-L	−811	−31	44	86	0.380	30	11.4

(1) S-L and D-L mean single-layer and double-layer structure, respectively.
(2) CTM, α-naphthalic hydrazone.
(3)TiOPc: α-NH:PC=1:14:10 (by wt.).
Thickness of a single-layer P/R is about 30 μm; to a double-layer P/R, the thicknesses of CGL and CTL are about 0.5 and 25 μm, respectively.
I exposure intensity.

On the other hand, a function-separated double-layer P/R is made, where CGL is TiOPc with a size of 281 nm dispersed in PC resin and CTL consists of α-NH and PC resin. The ratio of TiOPc, α-NH and PC in the device is the same (1:14:10, by wt.) as that in the single-layer device. It is found that, when compared to the single-layer P/R (same size of TiOPc particles), the double-layer P/R has bigger Rd, longer $t_{1/2}$, and higher $E_{1/2}$ under the exposure of 30 lux light intensity. It suggests that the photoconductivity of the single-layer P/R is better than that of the double-layer P/R. The result can also be explained in the view of the surface area of the CGM/CTM interface. The surface area of the CGM/CTM interface in the single-layer structure is obviously larger than that in the double-layer structure, leading to better photoconductivity.

Acknowledgements

This work was financed by the National Natural Science Foundation of China (No. 59603003 and 69890230).

References

[1] K.-Y. Law, Chem. Rev. 93 (1993) 449.
[2] M.O. Shattuck, U. Vahtra, U.S. Patent. 3,484,237 (1969).
[3] T. Enokida, R. Hirohashi, T. Nakamura, J. Imag. Sci. 34(6) (1990) 234.
[4] Y. Wang, N. Herron, J. Phys. Chem. 95 (1991) 525.
[5] T. Koyman, H. Miyazaki, H. Anayama, U.S. Patent 4,895,782 (1990).
[6] K.-Y. Law, I.W. Tarnawskyj, Z.D. Popovic, J. Imag. Sci. Tech. 38(2) (1994) 118.
[7] X. Zhang, S.A. Jenekhe, J. Perlstein, Chem. Mater. 8 (1996) 1571.
[8] F.H. Moser, A.L. Thomas, The Phthalocyanines, CRC, Boca Raton, FL, 1983.
[9] M. Wang, H.Z. Chen, S.L. Yang, J. Photochem. Photobiol. A: Chem. 88 (1995) 183.
[10] H.Z. Chen, M. Wang, S.L. Yang, J. Polym. Sci. A: Polym. Chem. 35 (1997) 959.
[11] M. Umeda, T. Niimi, M. Hashimoto, Jpn. J. Appl. Phys. 29 (1990) 2746.
[12] M. Umeda, T. Niimi, J. Imag. Sci. Tech. 38(3) (1994) 281.